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PHOTO-DESTRUCTION OF POLYMETHYL METHACRYLATE IN
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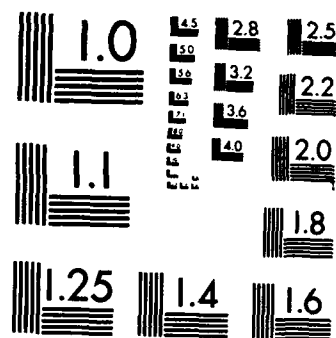
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PHOTO-DESTRUCTION OF POLYMETHYL METHACRYLATE IN SOLUTIONS

by

N.S. Kardash, V.A. Krongauz



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8 September 1987

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PHOTO-DESTRUCTION OF POLYMETHYL METHACRYLATE IN SOLUTIONS

By: N.S. Kardash, V.A. Krongauz

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Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

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However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as ѐ in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	\sinh^{-1}
cos	cos	ch	cosh	arc ch	\cosh^{-1}
tg	tan	th	tanh	arc th	\tanh^{-1}
ctg	cot	cth	coth	arc cth	\coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian English

rot curl
lg log

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PHOTO-DESTRUCTION OF POLYMETHYL METHACRYLATE IN SOLUTIONS.

N. S. Kardash, V. A. Krongauz.

During study of mechanism of photo-destruction of polymethyl methacrylate (PMMA) significant difficulty consists in the fact that PMMA absorbs in distant ultraviolet region, and in region of wavelengths ≥ 254 nm, emitted by light sources usually utilized in photochemistry, its absorption is actually conditioned on presence of admixtures/impurities of undetermined character. Therefore during irradiation of solid samples of PMMA it remains unclear, what groups or molecules initially absorb light and are the sources of primary active particles.

This difficulty it is possible to avoid, if we investigate destruction of PMMA in solutions, where solvent is absorbing component. Therefore in this work was investigated photolysis of the solutions of PMMA in the benzene under the effect of light from $\lambda = 253,7$ nm, virtually completely absorbed by benzene.

Photo-destruction of PMMA in benzene solutions under the effect of light with $\lambda \leq 265$ nm was investigated by Charlesby et al. [1]. It was established that in this system the speed of destruction does not depend on solution concentration with its change from 0.5 M to 10 M. On the basis of these data was made the conclusion that the

photo-destruction occurs as a result of the direct effect of light on the polymer. However, during the complete luminous absorption by system the speed of destruction must increase with an increase of polymer concentration in the solution. The independence of the speed of destruction from polymer concentration rather speaks about the indirect action of light, connected either with the energy transfer from the solvent to the polymer or with the reaction of polymer with the radicals, which are generated during irradiation of solvent.

PMMA was obtained by thermal-initiated polymerization of purified monomer in vacuum at 65° during 30 hours, and then they twice deposited from benzene solution by methanol. Molecular weight of the obtained polymer, calculated from the intrinsic viscosity according to formula $[\eta] = 7,6 \cdot M^{0,76} \cdot 10^{-5}$ [1], comprised $5 \cdot 10^4$.

As light source mercury-vapor lamp PRK-2, which worked because of intensive cooling in low-pressure regime/conditions and which gave virtually only line $\lambda = 254$ nm, served. Actinometry was determined on the decomposition of the solution of ferrioxalate complex [2]. The irradiation of benzene solutions of PMMA was conducted in the quartz cuvettes with a thickness of 1 cm. The quantum yields of destruction were calculated, on the basis of the gap count of chains of PMMA, determined from the change molecular weight of polymer before and after irradiation.

Fig. 1 shows dependence of quantum yields of breaks in chains of PMMA on its concentration in benzene solutions. From the figure it is evident that the quantum yields of breaks initially increase with an increase of the concentration of PMMA in the solution, and then they reach the limiting value, equal to $3.2 \cdot 10^{-4}$ breaks/quantum (portion of the light, absorbed directly by polymer, it does not exceed with the maximum concentration of polymer 10^{-4} from entire absorbed light). It is important to note that, in spite of the fact that the quantum yields are very small, they can be measured sufficiently reliably because of high molecular weight of polymer.

Obviously, destruction of PMMA cannot be caused by direct effect of light on polymer, since in this case quantum yields of destruction must monotonically increase/grow with increase of concentration of PMMA in solution, which in actuality is not observed. Therefore it is possible to assume that the destruction of PMMA occurs as a result of the indirect action of light on the polymer.

In order to explain, destruction of PMMA due to energy transfer of excitation from benzene does not occur to polymer, into solution of PMMA in benzene were introduced additives of organic phosphors: p-terphenyl and diphenyloxazole (RRO) - acceptors of energy during its transfer from benzene along singlet energy levels [3] and trans--stilbene, which decontaminates triplet excited states [4], in concentrations, sufficient for complete extinguishing of all generating singlet and triplet molecules of benzene. It seemed that

trans--stilbene not at all influences destruction of PMMA, but additives of RRO decrease the quantum yields of breaks in the chains of PMMA as this is shown by Fig. 2. Almost the same reduction in the quantum yields of destruction of PMMA occurs in the presence of p-terphenyl.

However, this reduction in quantum yields of breaks of PMMA in presence of additives of phosphors, apparently, is not connected with energy transfer from benzene to polymer on singlet levels, since it was established that PMMA in entire investigated region of concentrations does not extinguish luminescence of pure benzene, caused by light with $\lambda = 254$ nm.

Besides energy transfer destruction of PMMA can flow/occur as a result of reaction of PMMA with radicals, which are generated during irradiation of benzene. Actually, it seemed that the addition to the solutions of PMMA in the benzene of the acceptor of radicals DFPG in the concentration $5 \cdot 10^{-3}$ M virtually completely depresses destruction of PMMA. If we assume that the destruction is caused by radicals, becomes clear reduction in the outputs/yields of breaks in the chains of PMMA in the presence of diphenyloxazole and p-terphenyl, which, apparently, is caused by deactivation by the molecules of the phosphors of the excited singlet molecules of benzene to that how they will be decomposed into radicals [5]. This assumption is confirmed by the fact that the additions of diphenyloxazole and p-terphenyl to concentration 10^{-2} M decrease the yield of radicals from the pure

benzene approximately to 25-40%, i.e., to the same degree, in which they lower the quantum yields of destruction of PMMA.

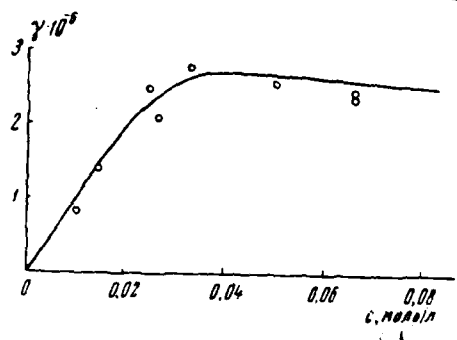


Fig. 1.

Fig. 1. Dependence of quantum yields of destruction of PMMA on its concentration in benzene solution.

Key: (1). mole/l.

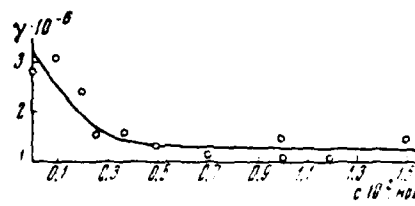


Fig. 2.

Fig. 2. Dependence of quantum yields of destruction of PMMA on concentration of RRO in solution. Concentration of PMMA is constant and equal to 0.033 M.

Key: (1). mole/l.

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The fact that formation of radicals of benzene and destruction of PMMA are not depressed completely in presence of diphenyl oxazole and p-terphenyl, is explained, apparently, by the fact that not all radicals of benzene are formed at fluorescent level. Possibly, the part of the radicals is formed from the molecules of benzene in the nonequilibrium states, which by diphenyloxazole and p-terphenyl are not intercepted. The quantum yield of free radicals measured according to the expenditure/consumption of DFPG from the benzene is equal to $2 \cdot 10^{-3}$, i.e., approximately three orders more than the output/yield of polymer destruction. Apparently, generating radicals

possess in this sense very little activity.

Authors thank Kh. S. Bagdasar'yan for attention to work.

Conclusions.

1. Photo-destruction of PMMA in benzene solutions under effect of light from $\lambda = 254$ nm, absorbed virtually completely by solvent, occurs as a result of reaction of PMMA with radicals, which are generated during irradiation of benzene.

2. Is possible formation of radicals from molecules of benzene, which are located not on fluorescent level, but in nonequilibrium states.

Scientific research physicochemical institute im. L. Ya. Karpov.

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